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## (54) VISIBLE LIGHT-ACTIVE PHOTOCATALYST PARTICLE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a visible light-active photocatalyst particle which, under the irradiation with visible light, exhibits a stable and persistent photocatalytic activity higher than that of a conventional one.

SOLUTION: The photocatalyst particle mainly comprises titanium dioxide, has been doped with nitrogen anion in a concentration of 700-10,000 wt.ppm and carbon anion in a concentration of 1/30-1/3 that of the nitrogen anion, and has a particle size of 1 μm or less. Its spectrum obtained by Fourier transform infrared spectroscopy has absorption peaks at wavenumbers of 340±10 cm-1 and 580±50 cm-1.

* NOTICES *



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## CLAIMS

[Claim(s)]
[Claim 1]
Visible photoactive mold photocatalyst grains, wherein a titanium dioxide is the main ingredients, it is the particles by which an anion of 700 or more wtppm nitrogen of 10000 or less wtppm and an anion of or more 1/30 1/3 or less carbon of said nitrogen concentration were doped and particle diameter of said particle is 1 micrometer or less.
[Claim 2]
Visible photoactive mold photocatalyst grains which a titanium dioxide is the main ingredients and are characterized by a spectrum measured by Fourier transform infrared spectroscopy having an absorption peak in wave number 340**10-$cm^{-1}$ and 580**50-$cm^{-1}$.
[Claim 3]
The visible photoactive mold photocatalyst grains according to claim 1 or 2 by which isopropanol oxidation activity being shown under the not less than 400-nm exposure [ 600 nm or less / visible light ] of wavelength.

[Translation done.]

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## DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]
About visible photoactive mold photocatalyst grains, more, in details, activity is shown to the exposure of visible light, and an operation disassembly of a toxic substance, deodorization, antibacterial properties, sterilization, antifouling, antifog is done so in them in this invention using such photocatalyst activity.
Therefore, it is related with the visible photoactive mold photocatalyst grains which can be used conveniently for detoxicating treatment agents, such as a paint, textiles, a sick house dissolution agent, waste industrial waters, exhaust gas, biomedical materials, etc.

[0002]
[Description of the Prior Art]
A photocatalyst has many things with semiconductor character, and a conducting zone and a valence band have the band structure separated by the band gap of suitable width.
If such a photocatalyst is irradiated with the light which has the energy more than the band gap, the electron of a valence band is excited by the conducting zone, and an electron hole will be produced in said valence band, and it will produce an electron in a conducting zone. The electron hole and electron which were produced here trigger an oxidation-reduction reaction, respectively.
Effects, such as disassembly of a toxic substance, deodorization, antibacterial properties, sterilization, and antifouling, can be demonstrated using the especially strong oxidizing power of them.
By the super-hydrophilic nature effect, since it becomes easy to adapt oneself to water, the antifog effect can also be demonstrated.
Therefore, taking advantage of the above effects, the application to a paint, textiles, a mirror, biomedical materials, etc. is proposed, and the part is already put in practical use now.
[0003]
By the way, in a titanium dioxide photocatalyst, there is mainly a crystal of an anatase type or a

rutile type, Since the band gap of a titanium dioxide is 3.2 eV (considerable in wavelength of 387.5 nm), or 3.0 eV (considerable in wavelength of 413.3 nm), respectively, as excitation light, With the wavelength of 387.5 nm or less or a wavelength of 413.3 nm or less short wavelength light, i.e., lights other than ultraviolet rays, was not used, respectively.

[0004]

However, in order to use sunlight efficiently, it is preferred that the visible light with a wavelength of 400-700 nm which occupies the most can be used.

The photocatalyst to which light energies, such as not only the outdoors but an indoor fluorescent lamp, react also in weak space is called for now.

For this reason, by these days, development of the titanium dioxide in which catalytic activity is shown by the exposure of visible light has come to be variously considered in order to use sunlight and artificial light efficiently.

[0005]

For example, by carrying out hydrogen plasma heat treatment of the anatase type titanium dioxide, an oxygen deficiency is formed in the patent documents 1, and the method of acquiring visible light activity is indicated.

It is indicated by doping nitrogen in the crystalline lattice of a titanium dioxide that a visible optical response is acquired (for example, refer to patent documents 2-4).

[0006]

In the above-mentioned oxygen deficiency type or the titanium dioxide by which the nitrogen dope was carried out, it is thought that visible light activity is brought to a titanium dioxide photocatalyst by combination of an oxygen deficiency defect or Ti-N.

[0007]

[Patent documents 1]

The patent No. 3252136 gazette

[Patent documents 2]

JP,2001-207082,A

[Patent documents 3]

JP,2001-72419,A

[Patent documents 4]

JP,2001-190953,A

[0008]

[Problem(s) to be Solved by the Invention]

However, the above-mentioned oxygen deficiency type and nitrogen dope type photocatalyst of the photocatalyst activity in a visible light exposure were low, and had technical problems, such as being inferior to stability.

[0009]

As a cause which such a technical technical problem produces, For example, the peak by the XPS (X-ray photoelectron spectroscopy) analysis based on Ti-N combination of a titanium dioxide by which the nitrogen dope was carried out, In the particle surface in contact with air, it is guessed from a certain thing that the report of having disappeared in the sample heat-

treated in the air is also what is depended on an oxygen deficiency defect or Ti-N combination being unstable.

[0010]

The purpose of this invention is as follows.

Be made in order to solve the above-mentioned technical technical problem, and high photocatalyst activity should be shown to a visible light exposure.

Provide the visible photoactive mold photocatalyst grains the photocatalyst activity excels [ photocatalyst grains ] in stability and durability.

[0011]

[Means for Solving the Problem]

Visible photoactive mold photocatalyst grains concerning this invention are the main ingredients, and a titanium dioxide An anion of 700 or more wtppm nitrogen of 10000 or less wtppm, It is the particles by which an anion of or more 1/30 1/3 or less carbon of said nitrogen concentration was doped, and is characterized by particle diameter of said particle being 1 micrometer or less.

Visible photoactive mold photocatalyst grains constituted in this way show more outstanding photocatalyst activity compared with a visible photoactive mold photocatalyst by a conventional oxygen deficiency type or a titanium dioxide by which the nitrogen dope was carried out, and, moreover, the photocatalyst activity is excellent in stability and durability.

[0012]

A spectrum which a titanium dioxide is the main ingredients and measured visible photoactive mold photocatalyst grains concerning this invention by Fourier transform infrared spectroscopy has an absorption peak in wave number 340**10-$cm^{-1}$ and 580**50-$cm^{-1}$.

The above-mentioned absorption peak in a Fourier transform infrared absorption spectrum (FT-IR) measured by the KBr method is based on nitrogen and carbon being doped, and, for this reason, photocatalyst activity outstanding under a visible light exposure is acquired.

[0013]

As for said visible photoactive mold photocatalyst grains, it is preferred that it is what shows isopropanol oxidation activity under the not less than 400-nm exposure [ 600 nm or less / visible light ] of wavelength.

By showing isopropanol (IPA) oxidation activity, it is corroborated that visible photoactive mold photocatalyst grains concerning this invention are what shows photocatalyst activity outstanding to a visible light exposure.

Therefore, visible photoactive mold photocatalyst grains concerning this invention, In the bottom of a visible light exposure by showing the above IPA oxidation activities, An outstanding function, such as disassembling and removing a substance which injures human bodies, such as environmental hormone, such as environmental pollutants, such as exhaust gas $NO_X$ etc. of aldehyde gas, such as formaldehyde called cause of sick house, and a car, and dioxin, can be exhibited.

[0014]

[Embodiment of the Invention]

Hereafter, this invention is explained more to details.

A titanium dioxide is the main ingredients and the visible photoactive mold photocatalyst grains concerning this invention are particles by which the anion of 700 or more wtppm nitrogen of 10000 or less wtppm and the anion of or more 1/30 1/3 or less carbon of said nitrogen concentration were doped.

Thus, the photocatalyst grains by which nitrogen and carbon were doped are compared with a conventional oxygen deficiency type or titanium dioxide photocatalyst by which the nitrogen dope was carried out, and the photocatalyst activity more outstanding under the visible light exposure is shown. And it excels in the photocatalyst activity stability and durability, and it is not easily deactivated even if it is a case where air is contacted.

The photocatalyst activity over UV irradiation also shows the conventional titanium dioxide photocatalyst and the performance more than comparable.

[0015]

The main ingredients in said visible photoactive mold photocatalyst grains are a titanium dioxide, as for the content, it is preferred that it is more than 80wt%, and it is more than 95wt% more preferably.

When the content of a titanium dioxide ingredient is less than [ 80wt% ], sufficient photocatalyst activity is not acquired.

Therefore, if it is a range below 20wt%, unless the photocatalyst activity by the visible light exposure of a titanium dioxide will be spoiled, the composite particle which mixed other inorganic compounds can also be used.

As an inorganic compound mixed by the titanium dioxide, silica, alumina, zirconia, magnesia, a zinc oxide, etc. can be mentioned, for example.

[0016]

Said titanium dioxide has a rutile type (pyramidal quadratic system), an anatase type (pyramidal quadratic system), and three sorts of brookite type (ortho rhombic system) transformations, and it has the structure where the oxygen atom configurated all six times in the titanium atom and where ** of the bent octahedron was shared. It is preferred to use a rutile type or anatase type thing from a viewpoint of making photocatalyst activity revealing, and an anatase type is [ in / this invention ] preferred especially.

[0017]

In this invention, visible photoactive mold photocatalyst grains are obtained by doping the anion of nitrogen and carbon to the particles which use this titanium dioxide as the main ingredients.

As for dopant concentration, about nitrogen, it is preferred that it is [ 700 or more wtppm ] 10000 or less wtppm, and it is 5000 or less wtppm of 1500 or more wtppm more preferably.

When the concentration of said nitrogen is less than 700 wtppm, sufficient photocatalyst activity over a visible light exposure may not be acquired, but moreover, the standup of initial activity is late especially, standup inclination may be small, and it may be difficult to fully attain

the purpose by visible luminous intensity, a use, etc.
As for the concentration of carbon, it is preferred that it is 1/3 or less [ of the concentration of a viewpoint to the above-mentioned nitrogen in which this also acquires sufficient visible light activity / 1/30 or more ].
[0018]
The doping method in particular of the anion of the above-mentioned nitrogen and carbon is not limited, and methods used in this kind of dope, such as a thermal diffusion method, the laser doping method, the plasma doping method, and ion implantation, are usually used for it, and it does not interfere.
Specifically, it can carry out using ion implantation equipment by the method of driving the acceleration ion from a nitrogen anion, the source of a carbon anion, etc. into a diacid-ized titanium target.
Cyanogen (HCN), cyanic acid, or isocyanic acid (HOCN), The solution containing low-grade amine ($RNH_2$, $R_2NH$, $R_3N$), azo, a diazo compound, etc., Or the method of hydrolyzing solution form halogenation titanium, such as a titanium chloride ($TiCl_4$), can also be used in the solution containing these and ammonia ($NH_3$). Or in inactive gas air currents, such as nitrogen or argon which contains these and ammonia, such as cyanogen, cyanic acid or isocyanic acid, and low-grade amine, again, Or it can carry out by the method of heat-treating a titanium dioxide (annealing), etc. in the mixed gas air current of various hydrocarbon and ammonia.
[0019]
Disassembly of a respectively different compound may perform the toe ping of nitrogen and carbon as mentioned above, and in this case, even when carbon and nitrogen are simultaneous, Or it may dope to serial and they may be any after the time of particle formation, or formation, corresponding to the mode also about a dope stage.
[0020]
The oxygen ion which has combined said titanium dioxide ($TiO_2$) with 1 mol of titanium ions stoichiometrically is 2 mol.
By doping the anion of nitrogen and carbon in this invention to the titanium dioxide which consists of such stoichiometrical chemical composition, It is preferred for the oxygen ion combined with 1 mol of titanium ions to have shifted rather than 2 mol which is the number of stoichiometries, namely, to consider it as the structure where it has a nonstoichiometric number.
By taking such a structure, a titanium dioxide is considered that it can demonstrate the high photocatalyst activity over a visible light exposure.
Specifically, oxygen ion united to 1 mol of titanium ions has preferred 1.9-mol or more thing become less than 2.0 mol.
[0021]
Therefore, as for the doped nitrogen anion, it is preferred to have combined with Ti of a titanium dioxide in the state, i.e., the integrated state of Ti-N-O, of entering between the lattices of the crystal of a titanium dioxide. Or oxygen under crystal of a titanium dioxide is replaced by

nitrogen, and, as for said doped nitrogen anion, it is preferred again to have combined with Ti of a titanium dioxide in the state, i.e., the integrated state of Ti-N-Ti, of going into the position of oxygen under titanium dioxide crystal.
It is more preferred that there is more Ti-N-Ti among these integrated states.
[0022]
The particle diameter of said visible photoactive mold photocatalyst grains shall be 1 micrometer or less from viewpoints of sufficient photocatalyst activity, the dispersibility to a solvent, etc., and is 0.01 micrometers or more 1 micrometer or less preferably. In particular, it is preferred that a primary particle has the shape of a with a not less than 10-nm major axis [ 100 nm or less ] spheroid. As for the major axis of said particle, it is more preferred that it is about 30-40 nm.
Since the titanium dioxide photocatalyst grains in such a size range are particles, they can be conveniently used for a paint use etc.
As for said primary particle, it is preferred that the ratio of a minor axis to a major axis is 1:2 to about four.
[0023]
The spectrum which measured the visible photoactive mold photocatalyst grains concerning this invention by Fourier transform infrared spectroscopy has an absorption peak in wave number 340**10-cm$^{-1}$ and 580**50-cm$^{-1}$.
In the Fourier transform infrared absorption spectrum (FT-IR) measured by the KBr method, that an absorption peak is observed near wave number [ of 340 cm ] $^{-1}$ and 580 cm$^{-1}$ means that nitrogen and carbon are doped.
With this nitrogen and carbon that were doped, the Ti-N combination in the visible photoactive mold photocatalyst grains concerning this invention is stable, and it can be said that the photocatalyst effect under a visible light exposure is large.
[0024]
Under the exposure of visible light, the visible photoactive mold photocatalyst grains concerning this invention show oxidation activities, such as formaldehyde and isopropanol (IPA).
The sample which carried out these photocatalyst grains 0.2g with the uniform layer for 10 cm around especially is put in in a gas bag with a capacity of 1 l., It is preferred that it is that from which the acetone gas concentration which generated the fluorescent lamp light which set isopropanol gas concentration to 1500ppm**150ppm at the beginning, and with which ultraviolet rays were shaded by said sample after a 1-hour exposure by intensity 0.5 mW/cm$^2$ in the wavelength of 420 nm is set to not less than 500 ppm.
If IPA oxidizes, it will generate acetone. Eventually, advance of oxidation reaction will generate carbon dioxide and water. Such oxidation reaction of IPA is used as one of the standard methods for evaluating photocatalyst activity.
[0025]
Generally, although photocatalyst product American Engineering Council's photocatalyst

performance evaluation test method IIb (the gas bag B method) is used as a photocatalyst activity valuation method of a titanium dioxide etc., this gas bag B method evaluates the photocatalyst activity by UV irradiation.

On the other hand, in this invention, in order to evaluate the photocatalyst activity over a visible light exposure, the above original evaluation test methods are adopted. Clarification of being what shows the photocatalyst activity in which the visible photoactive mold photocatalyst grains concerning this invention were excellent to the visible light exposure by this can be attained.

[0026]

Hereafter, the example of the photocatalyst activity evaluation test method of describing above the visible photoactive mold photocatalyst grains concerning this invention is explained.

First, make water distribute the photocatalyst grains 0.2g, apply this to a quartz glass plate (10 cm x 10 cm), and it is made to dry at 50 ** overnight, and let this be a test sample.

Next, after putting this test sample into a tedlar bag with a capacity of 1 l., the air having contained the isopropanol (IPA) steam is circulated in this tedlar bag for 1 hour, and the gas adsorption of photocatalyst grains is saturated.

The IPA gas concentration and acetone gas concentration in this tedlar bag are measured by a gas chromatography, and examination gas is prepared so that IPA gas concentration may be set to 1500ppm**150ppm and acetone gas concentration may be set to 0 ppm.

And the fluorescent lamp made to equip with the film which omits ultraviolet rays with a wavelength of 410 nm or less for said tedlar bag is used, The acetone gas concentration which generated the light of light intensity 0.5 $mW/cm^2$ in the wavelength of 420 nm by oxidation of IPA gas concentration and IPA after a 1-hour exposure is measured.

As for the visible photoactive mold photocatalyst grains concerning this invention, it is preferred that it is that from which the acetone gas concentration at this time is set to not less than 500 ppm, and they can specify that it is a photocatalyst which this shows the outstanding visible light activity.

[0027]

That a promotion operation of oxidation reaction of IPA under the exposure of the above visible light, i.e., IPA oxidation activity, is shown, Aldehyde gas, such as formaldehyde called cause of sick house, It means having the capability to disassemble and remove the substance which injures human bodies, such as environmental hormone, such as environmental pollutants, such as exhaust gas $NO_X$ of a car, and dioxin, and it can be said that the function outstanding as a visible photoactive mold photocatalyst is exhibited.

[0028]

[Example]

Hereafter, this invention is not restricted by the following example although this invention is explained still more concretely based on an example.

[Example]

The anatase type titanium dioxide particles (primary particle of the shape of a with the minor

axis of about 10 nm and a major axis of about 30 nm spheroid) which doped nitrogen 3000wtppm and carbon 150wtppm were compounded, and photocatalyst grains were produced.

[0029]

About the photocatalyst grains compounded in the above, the Fourier transform infrared absorption spectrum (FT-IR) by the KBr method was measured.

The product IFSmade from Bruker 113 V type and the Hitachi type 260-50 Fourier transform infrared spectrophotometer were used for the device, and resolution was measured by 4 $cm^{-1}$.

After mixing the test portion with KBr with the mortar and being powdered, what was made into the pellet type with the tablet molding machine was used.

The measured spectrum is shown in drawing 1 and drawing 2.

[0030]

The photocatalyst activity over visible light was evaluated about the above-mentioned photocatalyst grains. The visible photoactive evaluation test was done by the following method.

First, made water distribute the photocatalyst grains 0.2g compounded by the above, applied this to the quartz glass plate (10 cm x 10 cm), it was made to dry at 50 ** overnight, and this was made into the test sample.

Next, after putting this test sample into a tedlar bag with a capacity of 1 l., the air having contained the isopropanol (IPA) steam was circulated in the tedlar bag for 1 hour, the gas adsorption of photocatalyst grains was saturated, and examination gas was prepared.

When IPA of this examination gas and the gas concentration of acetone were measured by the gas chromatography (Shimadzu GC-8A, a column: Shimazu PAKKUDO column SBS-100), IPA was 1500 ppm and acetone had not been detected (ND).

And the fluorescent lamp (Toshiba FLR20S, W/M) equipped with the film (Fuji Photo Film, Inc. make UV Guard UGP20WL10) which shades ultraviolet rays with a wavelength of 410 nm or less for said tedlar bag is used, It irradiated with the light of light intensity 0.5 $mW/cm^2$ in the wavelength of 420 nm for 5 hours. The acetone gas concentration generated by oxidation of IPA gas concentration and IPA was measured every 30 minutes from the exposure start.

This result is shown in Table 1.

[0031]

[Comparative example]

About the conventional nitrogen dope type titanium dioxide particulate (made by A company) (primary particle diameter of 5-10 nm), the Fourier transform infrared absorption spectrum (FT-IR) was measured like the above-mentioned example.

The measured spectrum is shown in drawing 1 and drawing 2.

The photocatalyst activity over visible light was evaluated about this nitrogen dope type titanium dioxide particulate as well as the above-mentioned example.

This result is shown in Table 1.

[0032]

[Table 1]

| 照射時間 | | 照射前 | 30 分 | 60 分 | 90 分 | 300 分 |
|---|---|---|---|---|---|---|
| 実施例 | IPA(ppm) | 1500 | 1350 | 1100 | 800 | 0 |
| | アセトン(ppm) | ND | 350 | 880 | 1300 | 3300 |
| 比較例 | IPA(ppm) | 1500 | 1380 | 1280 | 1130 | 150 |
| | アセトン(ppm) | ND | 150 | 420 | 630 | 2000 |

[0033]
As shown in drawing 1 and drawing 2, the measurement result of FT-IR has an absorption peak in an example in wave number [ of 580 cm ] $^{-1}$, and 340 cm$^{-1}$, and it was accepted that the peak position differs from the comparative example in which only nitrogen was doped.
Said absorption peak is based on carbon and nitrogen which were doped.
In the visible photoactive mold photocatalyst grains concerning this invention, it is characteristic.

[0034]
As for the titanium dioxide photocatalyst grains (EXAMPLE) which doped the anion of nitrogen and carbon, the acetone gas generated by oxidation reaction of IPA was detected from the evaluation result shown in the above-mentioned table 1 by the exposure of visible light, and it was accepted that the photocatalyst activity over visible light is shown.
It was accepted that the photocatalyst concerning this this invention shows the photocatalyst activity superior to the nitrogen dope type conventional article (comparative example) from the generated amount of acetone by visible light exposure.
Change was not observed on the dark condition which does not irradiate with light.
[0035]
[Effect of the Invention]
While the visible photoactive mold photocatalyst grains concerning this invention show high photocatalyst activity to a visible light exposure compared with the conventional visible photoactive mold photocatalyst as above, the photocatalyst activity is excellent in stability and durability.
For this reason, the visible photoactive mold photocatalyst grains concerning this invention, It can use using the photocatalyst activity conveniently for various uses, such as detoxicating treatment agents, such as a paint, textiles, a sick house dissolution agent, waste industrial waters, exhaust gas, and biomedical materials, by doing so an operation disassembly of a toxic substance, deodorization, antibacterial properties, sterilization, antifouling, antifog.
[Brief Description of the Drawings]

[Drawing 1]The infrared absorption spectrum about the photocatalyst grains in an example and a comparative example is shown.

[Drawing 2]The infrared absorption spectrum about the photocatalyst grains in an example and a comparative example is shown.

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[Translation done.]